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(19) (CA) **CANADIAN PATENT** (12)

(54) Sublimation Transfer Imaging System

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Canada

SUBLIMATION TRANSFER IMAGING SYSTEMField of the Invention

This invention relates to a method of forming  
5 an image in which a sheet bearing a radiation-  
sensitive image-forming layer is image-wise exposed to  
record an image in said layer and thereafter the  
image-forming components are transferred to a receptor  
layer or sheet to form a permanent image. In  
10 particular, the invention relates to a sublimation  
transfer imaging process employing a  
radiation-sensitive sheet comprising one or more  
bleachable dyes.

Background of the Invention

15 Positive working non-silver systems in which  
an originally coloured species is decolourised  
(bleached) in an imagewise manner upon exposure to  
light have received a considerable amount of  
attention. A large variety of dyes and activators  
20 have been disclosed for such systems, see, for  
example, J. Kosar, Light Sensitive Systems, page 387,  
Wiley, New York 1965.

The reaction relies on the fact that the dye  
absorption is sensitising the dye's own destruction or  
25 decolourisation, for example a yellow dyes absorbs  
blue light; the excited dye thus formed reacts with an  
activator which releases the species to bleach the  
dye. Similarly green light would destroy the magenta  
and red light the cyan dyes.

30 This dye bleach-out process is thus capable of  
producing colour images in a simple way. However, in  
spite of its apparent simplicity, the bleach-out  
process poses a number of problems. In particular,  
the purity of the whites in the final image leaves



much to be desired, image stability may not be good and a fixing step may be required to stabilise the image.

Our copending European Patent Application No. 5 84301156.0 (Serial No. 0 120 601) discloses a radiation-sensitive element capable of recording an image upon image-wise exposure to radiation of selected wavelength, the element comprising, as the image-forming components, an effective amount of a 10 bleachable dye in reactive association with an iodonium ion.

The element is capable of recording a positive image simply upon exposure to radiation of selected wavelength; the radiation absorbed by the dye which is 15 in reactive association with an iodonium ion causes the dye to bleach. The dyes are believed to sensitise spectrally the reduction of the iodonium ion through the radiation absorbed by the dyes associated with the iodonium ion. Thereafter the element may be 20 stabilised to fix the image by destruction of the iodonium ion or by separation of the dye relative to the iodonium ion.

The dyes used may be of any colour and any chemical class which is capable of bleaching upon 25 exposure to radiation of selected wavelength in the presence of an iodonium ion.

By a suitable selection of dye an element may be prepared which is sensitive to radiation of a selected wavelength band within the general range 300 30 to 1100 nm, the particular wavelength and the width of the band depending upon the absorption characteristics of the dye. In general, where a dye has more than one absorption peak it is the wavelength corresponding to

the longest wavelength peak at which one would choose to irradiate the element.

Elements intended for the production of images from radiation in the visible region (400 to 700 nm) will contain dyes which will bleach from a coloured to a substantially colourless or very pale state. In practice, such bleachable dyes will undergo a change such that the transmission optical density at the  $\lambda_{\max}$  will drop from 1.0 or more to less than 0.09, preferably less than 0.05. The dyes will generally be coated on the support to provide an optical density of about 3.0 or more.

In the case of elements sensitive to ultraviolet radiation (300 to 400 nm) the dyes will not normally be coloured to the eye and there may be no visible change upon exposure to ultraviolet radiation and bleaching. The image-wise exposed elements may be used as masks for further ultraviolet exposure after fixing.

Infrared sensitive elements contain dyes having an absorption peak in the wavelength range 700 to 1100 nm. These dyes may also have absorption peaks in the visible region before and/or after bleaching. Thus, as well as providing a means for obtaining masks for subsequent infrared exposure in a similar manner to the ultraviolet masks, infrared sensitive elements may record a visible image upon image-wise exposure to infrared radiation.

Exposure may be achieved with a wide variety of sources including incandescent, gas discharge and laser sources. For laser scanning applications the laser beam may need to be focussed in order to achieve sufficient exposure.

The dyes used may be anionic, cationic or neutral. Anionic dyes give very good photo-sensitisation which is believed to be due to an intimate reactive association between the negatively charged dye and the positively charged iodonium ion. Also anionic dyes may readily be mordanted to cationic polymer binders and it is relatively simple to remove surplus iodonium ions in an aqueous bath in a fixing step if the mordanting polymer is cationic. However, neutral dyes also give good results and are preferred over cationic dyes for overall photosensitivity. Cationic dyes are least preferred since it is more difficult to achieve intimate reactive association between the positively charged dye and iodonium ion, and selective removal of iodonium ion after imaging is more difficult.

The bleachable dyes may be generically referred to as polymethine dyes which term characterises dyes having at least one electron donor and one electron acceptor group linked by methine groups or aza analogues. The dyes have an oxidation potential between 0 and +1 volt, preferably between +0.2 and +0.8 volt. The bleachable dyes may be selected from a wide range of known classes of dyes including allopolar cyanine dye bases, complex cyanine, hemicyanine, merocyanine, azine, oxonol, streptocyanine and styryl.

The dye and iodonium system has its greatest sensitivity at the  $\lambda_{\max}$  of the longest wavelength absorbance peak. Generally, it is necessary to irradiate the system with radiation of wavelength in the vicinity of this  $\lambda_{\max}$  for bleaching to occur. Thus, a combination of coloured dyes may be used, e.g.

yellow, magenta and cyan, in the same or different layers in an element and these can be selectively bleached by appropriate visible radiation to form a full colour image. Monochromatic or polychromatic  
5 images may be produced using the photosensitive materials with relatively short exposure times in daylight or sunlight or even artificial sources of light (e.g. fluorescent lamps or laser beams). The exposure time, for adequate results, for example when  
10 using an 0.5 kW tungsten lamp at a distance of 0.7 m, may be between 1 second to 10 minutes.

The iodonium salts used in the imaging system are compounds consisting of a cation wherein a positively charged iodine atom bears two covalently  
15 bonded carbon atoms, and any anion. Preferably the acid from which the anion is derived has a  $pK_a < 5$ . The preferred compounds are diaryl, aryl/heteroaryl or diheteroaryl iodonium salts in which the carbon-to-iodine bonds are from aryl or heteroaryl groups.  
20 Aliphatic iodonium salts are not normally thermally stable at temperatures above 0°C. However, stabilised alkyl phenyl iodonium salts such as those disclosed in Chem. Lett. 1982, 65-6 are stable at ambient temperatures and may be used.

25 The bleachable dye and iodonium salt are in reactive association on the support. Reactive association is defined as such physical proximity between the compounds as to enable a chemical reaction to take place between them upon exposure to light. In  
30 practice, the dye and iodonium salt are in the same layer or in adjacent layers on the support.

In general, the weight ratio of bleachable dye to iodonium salt in the element is in the range from 1:1 to 1:50, preferably in the range from 1:2 to 1:10.

The bleachable dye and iodonium salt may be applied to the support in a binder. Suitable binders are transparent or translucent, are generally colourless and include natural polymers, synthetic resins, polymers and copolymers, and other film forming media. The binders may range from thermoplastic to highly cross-linked, and may be coated from aqueous or organic solvents or emulsions.

Suitable supports include transparent film, e.g. polyester, paper e.g. baryta-coated photographic paper, and metallised film. Opaque vesicular polyester films are also useful.

The fixing of the radiation-sensitive elements may be effected by destruction of the iodonium ion by disrupting at least one of the carbon-to-iodine bonds since the resulting monoaryl iodine compound will not react with the dye. The conversion of the iodonium salt to its non-radiation sensitive form can be effected in a variety of fashions. Introduction of ammonia and amines in reactive association with the iodonium ion, or a reaction caused on heating, or UV irradiation of a nucleophilic anion such as  $I^{\ominus}$ ,  $Br^{\ominus}$ ,  $Cl^{\ominus}$ ,  $BAR_4^{\ominus}$  (tetra-arylboronide),  $ArO^{\ominus}$  (e.g. phenoxide), or  $4-NO_2C_6H_4CO_2^{\ominus}$ , with the iodonium ion, will effect the conversion.

An alternative method of achieving post-imaging stabilisation or fixing is to remove the iodonium ion from reactive association with the dye by washing with an appropriate solvent. For example, in the case of elements using mordanted oxonol dyes and water soluble iodonium salts formulated in gelatin, after imaging, the iodonium salt is simply removed by an aqueous wash, which leaves the immobilised dye in

the binder. The dye stability to light is then equivalent to that of the dye alone. An element in which the dye and iodonium salt is formulated in polyvinylpyridine may be treated with aliphatic  
5 ketones to remove the iodonium salt and leave the dye in the binder.

The elements may be used as transparencies for use with overhead projectors, for making enlarged or duplicate copies of colour slides and for related  
10 graphics or printing applications, such as pre-press colour proofing materials.

Dye diffusion transfer systems are known and are becoming increasingly important in colour photography (see C.C. Van de Sande in Angew Chem.  
15 1983, 22, 191-209). These systems allow "rapid access" colour images without a complicated processing sequence. The construction of these colour materials may be donor-receptor type (e.g. Ektaflex commercially available from Kodak) integral peel-apart type (e.g.  
20 Polaroid, E.H. Land, H.G. Rogers, V.K. Walworth in J. Sturge Nebelette's Handbook of Photography and Reprography, 7th Ed. 1977, Chapter 12), or integral single sheet type (e.g. Photog. Sci. and Eng., 1976, 20, 155). Silver halide diffusion transfer systems  
25 are also known (e.g. E.H. Land. Photog. Sci. and Eng., 1977, 21, 225). Examples of diffusion transfer fixing in non-silver, dye-forming reactions employing solvent application to effect the transfer are disclosed in United States Patent Specification Nos. 3 460 313 and  
30 3 598 583. The latter patent also describes a full-colour imaging element, applicable for preparation of colour proofs, fixed by transfer of dye precursors in register to a receptor. Other examples



of non-silver diffusion transfer imaging systems are disclosed in British Patent Specification Nos. 1 057 703, 1 355 618 and 1 371 898. The latter two Patents also disclose the transfer of dye images under  
5 the influence of dry heat.

It has now been found that certain dyes which are bleachable upon exposure to radiation in the presence of iodonium ion are susceptible to diffusion or sublimation transfer and this property may be  
10 utilised to separate such dyes from the iodonium ion and produce a clean, stable image by transfer from a radiation-sensitive layer to a receptor layer or separate receptor element.

Brief Summary of the Invention

15 According to the present invention there is provided a process for forming an image which comprises image-wise exposing to radiation of selected wavelength a carrier element comprising, as image forming components, in one or more imaging layers  
20 coated on a support a bleachable dye in reactive association with iodonium ion thereby bleaching the dye in exposed areas to form a positive image, and thereafter transferring the positive dye image to a receptor which is either a receptor layer present on  
25 the carrier or a separate receptor element by heating the carrier element to a sufficient temperature to allow the dye image to sublime to the receptor thereby forming an image on the receptor.

The process of the invention provides stable dye images, optionally full colour images, of high quality with low background fog. The imaging system does not require the presence of silver halide.

5        Description of the Preferred Embodiments

In accordance with the invention the bleachable dyes are sublimable and after image-wise exposure the carrier element is placed in intimate contact with a receptor and the resulting composite  
10 heated for a sufficient time and to a sufficient temperature to allow the dye to sublime across the interface to the receptor thereby forming a laterally reversed positive image on the receptor. Thereafter the carrier element is separated from the receptor.

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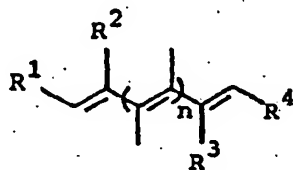
The sublimation transfer allows the formation of a stable dye image having high colour purity. The process is entirely dry and takes only a few minutes to give colour prints. A single transfer from the carrier element to a receptor results in a mirror image. If a true image, right-reading, is required a double transfer process may be employed transferring the dyes from the carrier element to an intermediate receptor and thereafter transferring the dyes from the intermediate receptor to the final receptor. Alternatively, a true image may be formed by reversing the transparency used for exposure.

The process may be used to achieve a multi-colour print either by sequentially transferring dyes from separate carrier elements or by utilising a carrier element having two or more coloured dyes, e.g. magenta, cyan and yellow, and transferring the dyes simultaneously.

Suitable dyes for use in this system are those which are both bleachable upon exposure to radiation in the presence of an iodonium ion and are sublimable, preferably in the temperature range 80 to 160°C, more preferably 100 to 150°C. In general, the dyes are electrically neutral (i.e. not charged) and have a molecular weight of less than 400, preferably less than 350. The dyes also generally possess a compact or "ball-like" structure; dyes having an elongate structure, e.g. those having long methine chains, do not readily sublime. The dyes are also selected such that they do not fade or undergo a change in colour on sublimation. When more than one dye is employed it is desirable to match the sublimation characteristics of the dyes to ensure an even transfer rate for all the dyes.

Suitable bleachable dyes may be generically referred to as polymethine dyes which term characterises dyes having at least one electron donor and one electron acceptor group linked by methine groups or aza analogues. The dyes have an oxidation potential between 0 and +1 volt, preferably between +0.2 and +0.8 volt. The bleachable dyes may be selected from a wide range of known classes of dyes including allopolar cyanine dye bases, complex cyanine, hemicyanine, merocyanine, azine, oxonol, streptocyanine and styryl.

In general, suitable dyes for use in the invention will have the structure:



in which:

n is 0, 1 or 2, and

$R^1$  to  $R^4$  are selected to provide an electron donor moiety at one end of the conjugated chain and an electron acceptor moiety at the other, and may be selected from substituents including hydrogen, halogen, cyano, carboxy, alkoxy, hydroxy, nitro, alkyl, aryl groups or heterocyclic rings any of which may be substituted. The skeletal structure of the groups  $R^1$  to  $R^4$  generally contain up to 14 atoms selected from C, N, O and S. When the skeletal structure of a  $R^1$  to  $R^4$  group is in the form of a linear chain there will usually be no more than 6 carbon atoms in the chain. When the skeletal structure is cyclic there will be no more than 7 atoms in any single ring. Cyclic structures may comprise two or more fused rings containing up to 14 atoms. If the skeletal structure of a  $R^1$  to  $R^4$  group comprises two unfused cyclic groups there will be no more than 3 atoms in the linear chain between the groups. Alternatively,  $R^1$  and  $R^2$  and/or  $R^3$  and  $R^4$  may represent the necessary atoms to complete optionally substituted aryl groups or heterocyclic rings, generally containing up to 14 atoms selected from C, N, O and S and having a structure as defined above.

The conjugated chain is preferably composed of carbon atoms but may include one or more nitrogen atoms providing the conjugation is not disrupted. The free valences on the chain may be satisfied by hydrogen or any substituent of the type used in the cyanine dye art including fused ring systems.

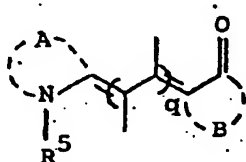
The particular selection of substituents  $R^1$  to  $R^4$  effects the light absorbance properties of the dye which may be varied to provide absorption peaks ranging from the ultraviolet (300 to 400 nm), near

visible (400 to 500 nm), far visible (500 to 700 nm) and infrared (700 to 1100 nm).

Dyes of the above formula are well known particularly in the silver halide photographic art and are the subject of numerous patents. Exemplary dye structures are disclosed in The Theory of the Photographic Process, T.H. James, Ed. MacMillan, Editions 3 and 4, and Encyclopaedia of Chemical Technology, Kirk Othmer, 3rd Edition, Vol. 18, 1983.

Within the above general structure of dyes are various classes of dye including:

1) Merocyanine dyes of the general formula:



in which:

$q$  is an integer of 0 to 2,

$R^5$  represents hydrogen or a substituent which may be present in conventional cyanine dyes, e.g. alkyl (preferably of 1 to 4 carbon atoms), etc.,

the groups A and B, which need not necessarily complete a cyclic structure with the methine chain, independently represent alkyl, aryl or heterocyclic groups or the necessary atoms to complete heterocyclic rings which may be the same or different. The skeletal structure of the groups A and B generally contain up to 14 atoms selected from C, N, O and S.

When the skeletal structure of A or B is in the form of a linear chain there will usually be no more than 6 carbon atoms in the chain. When the skeletal structure completed by A or B is cyclic there will be

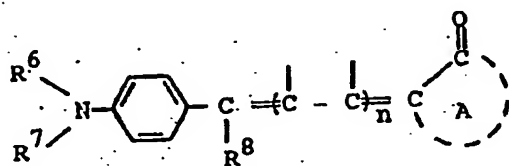
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no more than 7 atoms in any single ring. Cyclic structures may comprise two or more fused rings containing up to 14 atoms. If the skeletal structure complete by A or B comprises two unfused cyclic groups there will be no more than 3 atoms in the linear chain between the groups. Additionally B may complete a carbocyclic ring.

These dyes are well known in the silver halide photographic art and are described in The Theory of the Photographic Process, referred to above.

It is to be understood that these cyanine, merocyanine, anionic and oxonol dyes may bear substituents along the polymethine chain composed of C, N, O and S, and that these substituents may themselves join to form 5, 6 or 7 membered rings, or may bond with rings A and B to form further rings, possibly with aromatic character. Rings A and B may also be substituted by C, N, H, O and S containing groups such as alkyl, substituted alkyl, alkoxy, amine (primary, secondary and tertiary), aryl (e.g. phenyl and substituted phenyl), halo, carboxyl, cyano, nitro, etc. Exemplary substituents are well known in the cyanine dye art.

2) Benzylidene and cinnamylidene dyes of the structure:



in which:

A is as defined above, and may additionally be cyano, or carboalkoxy or other carbonyl-containing groups, e.g. ketone, or S=O containing groups, e.g. SO<sub>2</sub>Me,

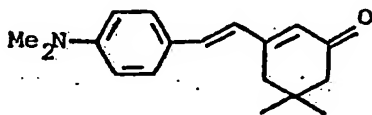
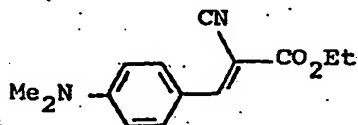
5 n is 0 or 1,

R<sup>6</sup> and R<sup>7</sup> independently represent a hydrogen atom or an alkyl group (optionally substituted) or aryl group containing up to 12 carbon atoms,

R<sup>8</sup> is H or CN or CO<sub>2</sub>R<sup>9</sup>, in which R<sup>9</sup> is an  
10 optionally substituted alkyl group of up to 6 carbon atoms, and

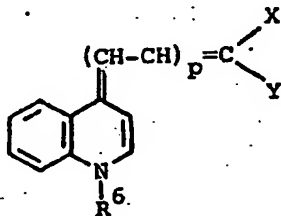
the free valences may be satisfied by hydrogen or alkyl groups, or together may form a 6-membered carbocyclic saturated or aromatic ring.

15 Examples of such dyes include:

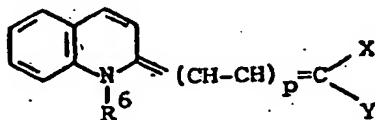


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3) Quinoline merocyanine dyes of the general structures:



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in which:

$R^6$  is as defined above,

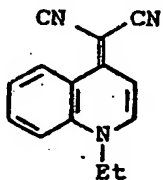
$p$  is 0 or 1, and

at least one of  $X$  and  $Y$  is an electron

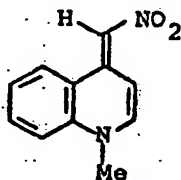
- 5 withdrawing group, e.g. cyano, nitro, carbonyl (in aldehyde, ketone, carboxylic acid, ester or amide), sulphonyl containing up to 6 atoms selected from C, N, O and S, or  $X$  and  $Y$  together form a 5 or 6 membered ring with additional atoms selected from C, N, O and S, and containing an electron withdrawing group (e.g. keto).
- 10

Examples of such dyes include:

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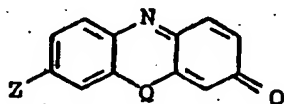
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- 4) Phenoazine dyes of the general structure:

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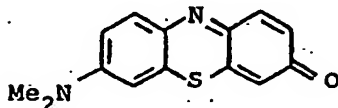
in which:

$Z$  is an electron donor, e.g.  $NR^6R^7$ , in which  $R^6$  and  $R^7$  are as defined above, and

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$Q$  represents O, S, NH,  $NCH_3$ ,  $NC_2H_5$ ,  $CH_2$ , e.g.

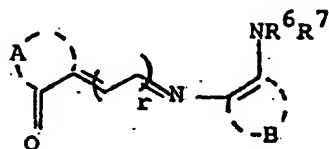
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5) Azamethine or indoaniline dyes of the general structure:



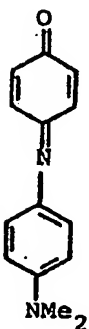
in which:

$r$  is 0 or 1, and

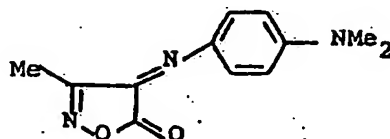
10  $A, B, R^6$  and  $R^7$  are as defined above.

The group  $NR^6R^7$  may also be positioned in a para-disposition to the chain, in addition to the ortho-disposition shown. Similarly the carbonyl group may be in other dispositions on the ring.

15 These dyes have been used in chromogenic photographic processes. Specific examples of such dyes include:



and



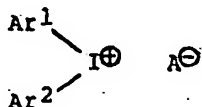
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The iodonium ions used in the invention are compounds consisting of a cation wherein a positively charged iodine atom bears two covalently bonded carbon atoms, and any anion. The preferred compounds are

5 diaryl, aryl/heteroaryl or diheteroaryl iodonium salts in which the carbon-iodine bonds are from aryl or heteroaryl groups and one of the aryl or heteroaryl groups is substituted with an alkyloxy group.

Suitable iodonium salts may be represented by the

10 formula:



15 in which:

Ar<sup>1</sup> and Ar<sup>2</sup> independently represent carbocyclic or heterocyclic aromatic-type groups generally having from 4 to 20 carbon atoms, or together with the iodine atom complete a heterocyclic

20 aromatic ring.

These groups include substituted and unsubstituted aromatic hydrocarbon rings, e.g. phenyl or naphthyl, which may be substituted with alkyl groups, e.g. methyl, alkoxy groups, e.g. methoxy, chlorine,

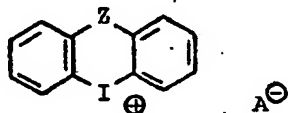
25 bromine, iodine, fluorine, carboxy, cyano or nitro groups or any combination thereof. Examples of hetero-aromatic groups include thienyl, furanyl and pyrazolyl which may be substituted with similar substituents as described above. Condensed

30 aromatic/hetero-aromatic groups, e.g. 3-indolinyl, may also be present,

A<sup>⊖</sup> represents an anion which may be incorporated into Ar<sup>1</sup> or Ar<sup>2</sup>.

Preferably Ar<sup>1</sup> and Ar<sup>2</sup> do not have more than two substituents at the alpha-positions of the aryl groups. Most preferably Ar<sup>1</sup> and Ar<sup>2</sup> are both phenyl groups.

5 The alpha-positions of the Ar<sup>1</sup> and Ar<sup>2</sup> groups may be linked together to include the iodine atom within a ring structure, e.g.



in which Z is an oxygen or sulphur atom. An example of such an iodonium salt is:

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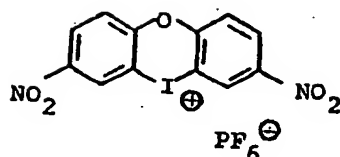
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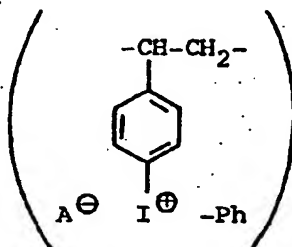
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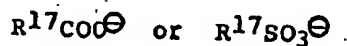
Other suitable iodonium salts include polymers containing the unit:



in which Ph represents phenyl.

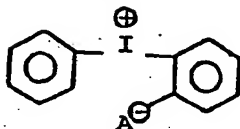
Examples of such polymers are disclosed in Yamada and Okowara, Makromol. Chemie, 1972, 152, 61-6.

Any anion may be used as the counter-ion  $A^-$  provided that the anion does not react with the iodonium cation under ambient temperatures. Suitable inorganic anions include halide anions,  $HSO_4^-$ , and halogen-containing complex anions, e.g. tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate and hexafluoroantimonate. Suitable organic anions include those of the formulae:



30 in which  $R^{17}$  is an alkyl or aryl group of up to 20 carbon atoms, e.g. a phenyl group, either of which may be substituted. Examples of such anions include  $CH_3COO^-$  and  $CF_3COO^-$ .

$A^{\ominus}$  may be present in  $Ar^1$  or  $Ar^2$ , e.g.



in which  $A^{\ominus}$  represents  $COO^{\ominus}$ , etc.

Furthermore,  $A^{\ominus}$  may be present in a molecule containing two or more anions, e.g. dicarboxylates  
 10 containing more than 4 carbon atoms.

The most significant contribution of the anion is its effect upon the solubility of the iodonium salt in different solvents or binders.

Most of the iodonium salts are known, they may  
 15 be readily prepared and some are commercially available. The synthesis of suitable iodonium salts is disclosed in F.M. Beringer et al, Journal of the American Chemical Society, 80, 4279 (1958).

Suitable substrates for the donor (or carrier)  
 20 for use in sublimation transfer are plastics film, paper (cellulosic or synthetic fibre), metallised plastics film and plastic film to film or plastic film to paper laminates.

The substrate should be unaffected by the  
 25 processing conditions. For example, the substrate must be heat-stable and not possess undesirable dimensional variation, nor degradation, nor tackiness when subjected to the sublimation conditions. A preferred substrate is a plastics film such as  
 30 polycarbonate film, cellulose acetate film or most preferably polyester, e.g. poly(ethylene terephthalate), which may be biaxially orientated.

The substrates may possess surface modifying or other coatings to enhance adhesion of imaging layers, to improve smoothness, etc. Resin coated photographic grade paper is a suitable substrate. The  
5 plastics film may specifically possess a subbing layer which acts as a priming layer for gelatin and other hydrophilic coating.

Binders suitable for use in preparing the carrier element for use in sublimation transfer are  
10 organic binders which dissolve readily in solvent and afford on coating clear dispersions of the dyes and iodonium salts described herein. Suitable binders include poly(vinyl butyral), poly(vinyl acetate) polymers and phenolic resins. The preferred weight  
15 range of iodonium ion to binder is from 3 to 15%. The preferred weight range of dye to iodonium salt is 1:1 to 1:15, more preferably 1:1 to 1:5.

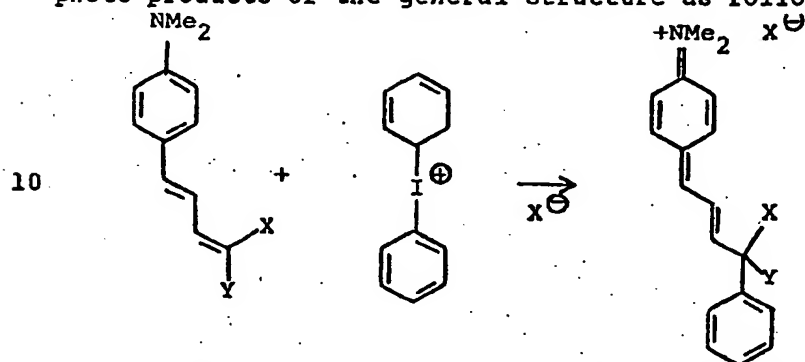
The binder must allow the dyes to migrate on heating to the processing temperature, thus allowing transfer to the receptor layer. If more than one dye is present, a general equivalence of sublimation transfer rates is desirable.

A layer containing the above components is coated preferably at 30 to 60 g/m<sup>2</sup>, wet deposition onto the substrate. It is undesirable to have overlayers as this hinders sublimation of the dyes, unless the overlayer is very thin. It is also preferred for all the bleachable dyes and iodonium salts present in an element to be in a single layer. Generally the element should be constructed so as not to inhibit the ready sublimation transfer of the dye from the carrier sheet. The topmost surface of the element should allow good contact with the receptor layer and not become tacky on heating to the transfer temperature.

The carrier element is firstly exposed so as to cause bleaching of the dyes by reaction with the iodonium ion. Most frequently visible light will be used, the actinic wavelengths corresponding to the absorption characteristics of the dyes. A variety of light sources may be used including continuous white light and laser. Sufficient exposure must be given to ensure full bleaching or decomposition of the dyes, as residual, unreacted dye may transfer. Thereafter the exposed precursor element is used to effect transfer of the unreacted dyes. Exposure is normally undertaken at ambient conditions of temperature although mild heating is allowable generally up to about 80°C, provided that this does not cause sublimation.



On light exposure the dyes react with the  
 iodonium ions to give non-sublimable, charged  
 species. The dyes reported in Table 1 are believed to  
 react on exposure with iodonium salts to give charged  
 5 photo-products of the general structure as follows:



The reaction products do not significantly  
 transfer on heating. After imaging at room  
 temperature, the unbleached dye is readily separated  
 by thermal transfer. Thus, the unbleached dye is  
 transferred by sublimation to the receptor, and the  
 20 iodonium salt and the dye photoproduct remain  
 substantially in the imaging layer.

While the main purpose of this invention is to  
 achieve visible dye transfer, organic ultraviolet and  
 infrared absorbing molecules may also be transferred,  
 25 e.g. to make ultraviolet or infrared masks.

The receptor material may be selected from a  
 wide range of materials as described above including  
 paper, particularly coated paper, e.g. poly(vinyl  
 chloride) coated paper, plastics film materials, e.g.  
 30 polyester, such as poly(ethylene terephthalate) films,  
 including metallised films, woven and non-woven  
 materials such as textile fabric and cloth and  
 plastics paper.

The precursor and receptor should be capable of conforming together to allow transfer. The receptor material should absorb the transferred dyes for permanence and may be coated with absorbing  
5 pigments, mordants and organic polymers to improve dye absorption and stability. The receptor should withstand the transfer conditions and not exhibit adverse loss of dimensional stability or tackiness.

Typical processing times are from 30 to 120  
10 seconds, with heating from 100 to 150°C. Thereafter the receptor is separated giving a single or multiple (e.g. full) colour reproduction. Heat may be applied through conduction or convection, contact with a heated roller, drum, platen or other surface, or in an  
15 oven or by an electrically heated layer or underlayer.

The short processing time and dry conditions are particularly useful aspects of this invention. The choice of receptor substrates is large and the transfer leaves behind various species which  
20 contribute to background fog levels. The backgrounds on the receptors are much cleaner (e.g. low  $D_{min}$ ) and there is a reduced tendency for the dye to degrade, being removed from the proximity of iodonium ions.

Dyes transferred to a receptor substrate may  
25 be further transferred from the receptor to yet another receptor. Here if the transfer is to be effected again, the first receptor should readily release the dyes again on heating. Multiple transfers of this kind will generally be accompanied by some  
30 loss in resolution and optical density. Single transfer results in a reversed-reading image. Double transfer results in a right-reading image.

Dyes may be transferred sequentially from

separate substrates in order to achieve a multi-colour print, but generally it is desirable to transfer magenta, cyan and yellow dyes simultaneously from a single substrate if a full-colour print is required.

5        Once transferred the dyes may be viewed by reflection, as on paper, or by transmission. In general, only the unreacted dyes are transferred, however it is permissible for sublimable colourless stabilising additives to be transferred. Preferably  
10 such additives are incorporated in the surface of the receptor. Additives allowing maintenance of colour density are particularly useful.

The invention will now be illustrated by the following Examples.

15        In the following Examples the sensitivity of the element was measured by the following technique. A 2.5 cm square piece of each sample was exposed over an area of 2.5 mm<sup>2</sup> with focussed light filtered, using a Kodak narrow band filter (551.4 nm: power output =  
20 2.36 x 10<sup>-3</sup> W/cm<sup>2</sup>) and the change in the transmission optical density with time was monitored using a Joyce Loebel Ltd. microdensitometer. A plot of transmission optical density versus time was made and the exposure time (t) for the optical density to fall from D<sub>max</sub> to  
25 (D<sub>max</sub>-1) was determined. The energy required (E) was calculated as the exposure time (t) x power output (= 2.36 x 10<sup>-3</sup> W/cm<sup>2</sup>): this gives an indication of the sensitivity of the elements.

In all cases a significant reduction of  
30 background density was achieved after transfer which gave a much cleaner image. Typically the minimum density before transfer and after exposure was approximately 0.15, this reducing to approximately 0.05 or below after transfer.

Example 1Single dye sublimation transfer

Dye No. 1 (0.06 g) in 3 ml ethanol was added to Butvar<sup>\*</sup> B76 (1 g) in 7 ml butan-2-one. Diphenyliodonium hexafluorophosphate (0.3 g) was added to the resulting lacquer in red light. The mixture was coated at 75 micron thickness on unsubbed polyester base and dried at room temperature for 15 minutes in the dark. The following Table reports the initial and transferred maximum optical densities, D<sub>max</sub>, achieved.

A strip of the sample was imaged through a step wedge having an optical density differential between adjacent steps of 0.15, with a tungsten halide source (1 kW, 0.5 m) for 120 seconds. The resulting step image was contacted with a photographic, baryta paper receptor coated with poly(vinyl chloride) Bakelite Ltd., type VVNS, in the dark. The construction was covered with muslin and the composite heated with an iron set at "cotton" (temperature 150°C) for 2 minutes. Separation of the construction gives a "mirror image" copy of the carrier film transferred onto the PVC coated paper. The following Table reports the reflected density after transfer. The minimum background density was found to be significantly less after the transfer process.

Resolution test

A strip of the sample was contacted with an UGRA mask (the UGRA mask was an 1976 UGRA-Gretag-Plate Control Wedge PCW) and this construction imaged as above using a tungsten halide source. In the carrier, the best resolution was 4 micron which is equivalent to 250 lines per millimetre. The image was

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transferred to the PVC coated receptor by heating as above described. The best resolution was 17 micron which is equivalent to 59 lines per millimetre.

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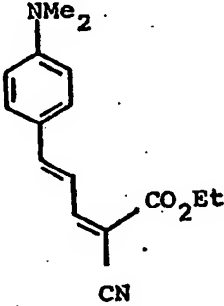
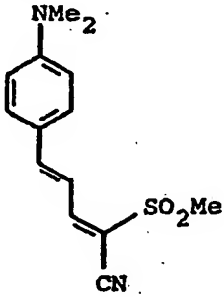
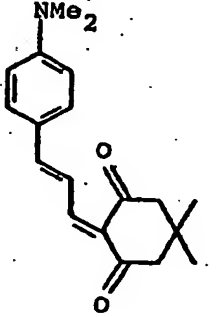
Examples 2 to 6

Example 1 was repeated using the dyes reported in the following Table, individually in the proportions indicated. The Table reports the maximum  
10 optical density by transmission achieved in the original and by reflectance in the receptor and the energy required at the max of the dye which gives a measure of the photosensitivity of the composition. A  
15 density was observed after sublimation transfer.

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Table

Example No.	Dye No.	Structure	Weight g	$\lambda_{\text{max}}$ in ethanol nm	Density		$E$ ( $\times 10^6$ mJ/m <sup>2</sup> )
					Ini	Tr	
1	1		0.06	475	1.5	1.0	1.9
2	2		0.06	450	1.3	0.9	8
3	3		0.06	550	1.3	1.3	6.2

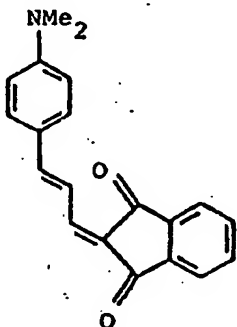
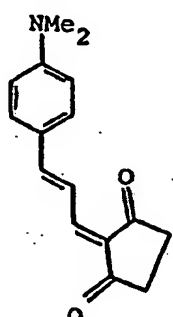
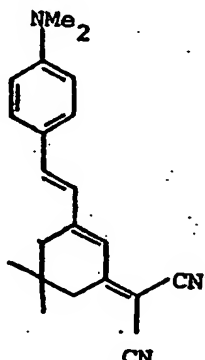
Ini = Initial density (transmission)

Tr = Transferred density (reflected) after heating  
2 mins/150°C.

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Table (Contd.)

Example No.	Dye No.	Structure	Weight g	$\lambda_{\text{max}}$ in ethanol nm	Density Ini	Tr	$E$ ( $\times 10^6$ mJ/m <sup>2</sup> )
4	4		0.06	570	1.0	0.8	5.1
5	5		0.06	560	1.3	1.2	7.6
6	6		0.06	503	0.9	0.5	6

Examples 7 to 14Photothermographic imaging with sublimation fixing

5        These Examples are for dyes which need light and heat simultaneously to react with iodonium salts.

         The samples were coated in Butvar as in Example 1, but containing the dyes in the following Table, in the reported amounts. These dyes do not  
10 react with iodonium salts at room temperature, e.g. the change in the dye absorbance is zero after 5 minutes exposure to filtered light (2 mm<sup>2</sup> spot/1.7 mW/cm<sup>2</sup>). On heating to above the T<sub>g</sub> of the binder, e.g. 70°C for Butvar B76, the  
15 light-induced reaction occurs. In some cases, there is an intermediate colour prior to bleaching.

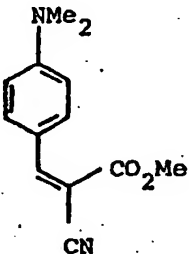
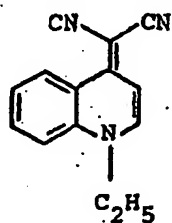
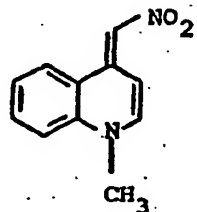
         In all cases a significant reduction in the minimum background optical density was observed.



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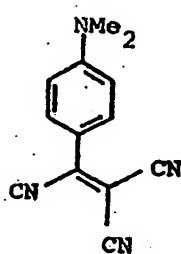
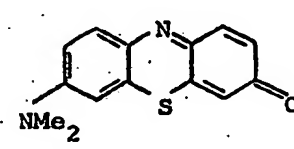
Table

Example No.	Dye No.	Structure	Weight g	$\lambda_{\text{max}}$ in a) ethanol b) Butvar nm	Density		$E$ ( $\times 10^6$ mJ/m <sup>2</sup> )	
					Ini	Tr	25°C	80°C
7	7		0.04	430 a	3.0	1.8	400	9
8	8		0.02	430 b	1.2	0.8	90	0.7
9	9		0.02	470 b	0.9	0.4	100	9

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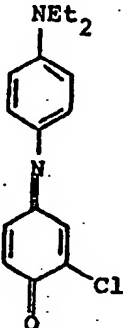
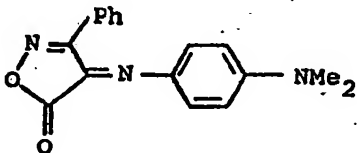
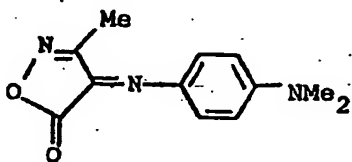
Table (Contd.)

Example No.	Dye No.	Structure	Weight g	$\lambda_{\text{max}}$ in a) ethanol b) Butvar nm	Density ini Tr	E ( $\times 10^6$ mJ/m <sup>2</sup> )	
						25°C	80°C
10	10		0.04	550 a	0.5 0.6	100	80
11	11		0.02	560 a 600 b	0.6 0.7	50	-

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Table (Contd.)

Example No.	Dye No.	Structure	Weight g	$\lambda_{\max}$ in a) ethanol b) Butvar nm	Density		$E$ ( $\times 10^6$ mJ/m <sup>2</sup> )	
					Ini	Tr	25°C	80°C
12	12		0.02	660 a	0.5	0.6	100	1.3
13	13		0.02	540 a	0.9	0.2	100	9
14	14		0.10	530 a	1.8	1.2	100	1.8

Ini = Initial density (transmitted)

Tr = Transferred density (reflected) after heating  
2 mins/150°C.

Example 15Light and heat imaging fixed by transfer

5        The blue coating of Example 12 was contacted with a black on white photocopy and the composite put through the 3M Thermofax Model 45CB processor at the "medium" setting. The result was a negative copy of the photocopy, bleaching had occurred in the regions  
10 in contact with the black characters. This copy was then stabilised by dye sublimation to a poly(vinyl chloride) coated paper receptor by heating for 30 seconds at 100°C. The result was a blue-coloured negative print of the original. A significant  
15 reduction in background density was observed on transfer.

Example 16

20        This Example shows the single sheet panchromatic capability of the invention.

      A mixture of Dye No. 1 (0.06 g) and Dye No. 13 (0.06 g) in 3 ml EtOH was added to a lacquer of Butvar B76 (1 g) in 7 ml butan-2-one. To the red mixture in  
25 red light, was added diphenyliodonium hexafluorophosphate (0.3 g). The resulting lacquer was knife-edge coated at 75 micron, wet thickness onto unsubbed polyester base (100 micron). The film was dried for 15 minutes at room temperature in air.

30        A strip of this red film was subjected to a spot of light filtered through a narrow cut filter at 551.4 nm for 100 seconds; in the area of light, a yellow spot (5 mm diameter) formed. The imaged strip

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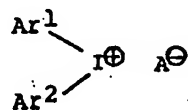
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was then contacted with PVC coated paper and the composite heated for 2 minutes at 150°C to transfer the dyes out of Butvar layer into the receptor. Good resolution was obtained; there was no spread of magenta into the imaged yellow spot.

## CLAIMS:

1. A process for forming an image which comprises image-wise exposing to radiation of selected wavelength a carrier element comprising, as image forming components, in one or more imaging layers coated on a support a bleachable dye in reactive association with iodonium ion thereby bleaching the dye in exposed areas to form a positive image, and thereafter transferring the positive dye image to a receptor which is either a receptor layer present on the carrier or a separate receptor element by heating the carrier element to a sufficient temperature to allow the dye image to sublime to the receptor thereby forming an image on the receptor.

2. A process as claimed in Claim 1, in which the iodonium compound has the general formula:

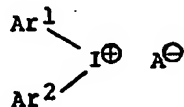


in which:

Ar<sup>1</sup> and Ar<sup>2</sup> independently represent carbocyclic or heterocyclic aromatic-type groups having 4 to 20 carbon atoms, or together with the iodine atom complete a heterocyclic aromatic ring, and A<sup>⊖</sup> represents an anion which may be incorporated into Ar<sup>1</sup> or Ar<sup>2</sup>.

## CLAIMS:

1. A process for forming an image which comprises image-wise exposing to radiation of selected wavelength a carrier element comprising, as image forming components, in one or more imaging layers coated on a support a bleachable dye in reactive association with iodonium ion thereby bleaching the dye in exposed areas to form a positive image, and thereafter transferring the positive dye image to a receptor which is either a receptor layer present on the carrier or a separate receptor element by heating the carrier element to a sufficient temperature to allow the dye image to sublime to the receptor thereby forming an image on the receptor.
2. A process as claimed in Claim 1, in which the iodonium compound has the general formula:



in which:

Ar<sup>1</sup> and Ar<sup>2</sup> independently represent carbocyclic or heterocyclic aromatic-type groups having 4 to 20 carbon atoms, or together with the iodine atom complete a heterocyclic aromatic ring, and A<sup>⊖</sup> represents an anion which may be incorporated into Ar<sup>1</sup> or Ar<sup>2</sup>.

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3. A process as claimed in Claim 2, in which the carrier element comprises cyan, magenta and yellow bleachable dyes, the element being constructed and arranged to allow even transfer of each dye.

5

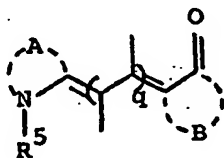
4. A process as claimed in Claim 2, in which the dye and iodonium salt are present in one or more layers in a polymeric binder, the weight ratio of dye to iodonium salt being in the range of from 1:1 to 1:50 and the binder is present in an amount from 50 to 98% by weight of the total weight of binder, dye and iodonium salt.

5. A process as claimed in Claim 2, in which the bleachable dyes are sublimable within the temperature range from 100 to 150°C and the process comprises placing the carrier element in contact with a receptor and heating to a temperature of 100 to 150°C for a period of about 30 to 120 seconds to transfer the dye image from the carrier element to the receptor.

6. A process as claimed in Claim 5, in which the bleachable dye is selected from

a) merocyanine dyes of the general formula:

25



30



in which:

q is an integer of 0, 1 or 2,

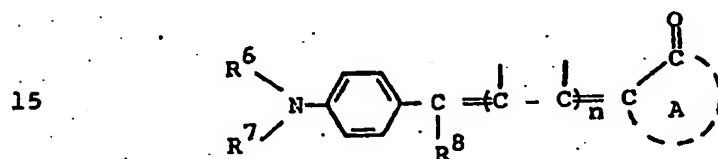
R<sup>5</sup> represents a hydrogen atom or substituents which may be present in conventional cyanine dyes,

5 A represents an alkyl, aryl or heterocyclic group or the necessary atoms to complete a heterocyclic ring, and

B is selected from the same groups as A or additionally may complete a carbocyclic ring,

10

b) benzylidene and cinnamylidene dyes of the structure:



in which:

A is as defined above, and may additionally be  
20 cyano, or carboalkoxy or other carbonyl-containing groups, or S=O containing groups,

n is 0 or 1,

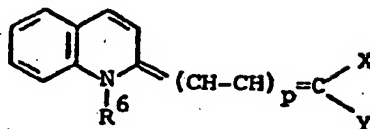
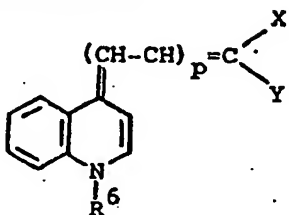
R<sup>6</sup> and R<sup>7</sup> independently represent a hydrogen atom or an alkyl group (optionally substituted) or  
25 aryl group containing up to 12 carbon atoms,

R<sup>8</sup> is H or CN or CO<sub>2</sub>R<sup>9</sup>, in which R<sup>9</sup> is an optionally substituted alkyl group of up to 6 carbon atoms, and

the free valences may be satisfied by hydrogen  
30 or alkyl groups, or together may form a 6-membered carbocyclic saturated or aromatic ring,

**40**

5



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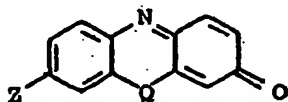
$R^6$  is as defined above,

at least one of X and Y is an electron

15 withdrawing group, sulphonyl containing up to 6 atoms selected from C, N, O and S, or X and Y together form a 5 or 6 membered ring with additional atoms selected from C, N, O and S, and containing an electron withdrawing group,

20.

d) ... phenoazine dyes of the general structure:



25

**Z is an electron donor,**

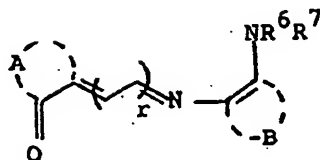
Q represents O, S, NH, NCH<sub>3</sub>, NC<sub>2</sub>H<sub>5</sub>, CH<sub>2</sub>,

30

**and**

15

e) azamethine or indoaniline dyes of the general structure:



in which:

r is 0 or 1, and

10 A, B, R<sup>6</sup> and R<sup>7</sup> are as defined above, the NR<sup>6</sup>R<sup>7</sup> and carbonyl group optionally being in other dispositions on the rings A and B.

7. A process as claimed in Claim 6, in which the  
15 process comprises the additional step of placing the receptor in intimate contact with a final receptor and heating the composite for a sufficient time and to a sufficient temperature to allow the dye to sublime across the interface to the final receptor thereby  
20 forming a true image.

8. The combination of a radiation-sensitive carrier element comprising, as image-forming components, one or more imaging layers coated on a  
25 support, a bleachable sublimable dye in reactive association with iodonium ion and a separate receptor element comprising a substrate having coated thereon a receptor layer comprising a polymeric binder.

30

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